

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

Leenders et al.

Application No. Unassigned

Filed: October 24, 2003

Art Unit: Unassigned

Examiner: Unassigned

For: PROCESS FOR THE OFFSET PRINTING OF PATTERNS VIA  
THE FOUNTAIN MEDIUM

**CLAIM OF PRIORITY**

Mail Stop Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

In accordance with the provisions of 35 USC 119, Applicants claim the priority of the following application or the applications (if more than one application is set out below):

Application No. 02102518.4, filed in the European Patent Office on October 31, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,



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Date: October 24, 2003





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**Bescheinigung**

**Certificate**

**Attestation**

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

02102518.4

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**





Anmeldung Nr:  
Application no.: 02102518.4  
Demande no:

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Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se referer à la description.)

Process for the offset printing of patterns of intrinsically conductive polymers

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
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AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR



## DESCRIPTION

## Field of the invention

5       The present invention relates to a process for the offset printing of patterns of intrinsically conductive polymers.

## Background of the invention.

10       Lithographic printing presses use a so-called printing master such as a printing plate which is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a print is obtained by applying ink to the image and then transferring the ink from the master onto a receiver material,  
15 which is typically paper. In conventional lithographic (offset) printing, both ink and an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-  
20 accepting, ink-repelling) areas. In so-called driographic printing, the lithographic image consists of ink-accepting and ink-abhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

      Plate materials include those based on UV-exposure through a  
25 mask or image-wise exposure with a laser followed by processing with solubilization in the case of positive plates or insolubilization in the case of negative plates, and those for processing using laser-ablation techniques, such as used in typical computer-to-plate plates or plate materials which are not ablative  
30 and do not need wet processing. Known examples of such non-ablative processless plate materials contain a so-called 'switchable' image-recording layer, i.e. a layer of which the affinity towards ink or an ink-abhesive fluid can be converted upon image-wise exposure from one state to the opposite state, e.g. from hydrophilic to  
35 oleophilic or from ink-accepting to ink-abhesive. Such materials are based on

      - switchable polymers (e.g. EP 924 102) which can be image-wise converted from a hydrophobic state to a hydrophilic state (W092/09934; EP 652 483) or vice-versa (US 4,081,572; EP 200  
40 488; EP 924 065);

- thermally induced coalescence of thermoplastic polymer particles in a crosslinked binder (US3,476,937; EP-A 882 583; Research Disclosure no. 33303); and
- thermally induced rupture of microcapsules and the subsequent  
5 reaction of the microencapsulated oleophilic compounds with functional groups on cross-linked hydrophilic binders (US 5,569,573; EP 646 476; EP 949 088).

In offset printing a fountain solution and then the ink are applied to the printing plate on a drum and they are transferred to  
10 an intermediate (rubber) roll, known as the offset blanket, from which they are printed onto paper sheets transported between the impression cylinder and the intermediate (rubber) roll.

The fountain solution is transferred via a series of rolls to the printing plate or a fine emulsion of ink and the fountain  
15 solution are prepared on an ink roll which is then applied to the plate. The fountain solution conventionally acts as a weak sacrificial layer and prevents ink from depositing on the non-image area of the plate and has the function of rebuilding the non-printing (desensitized) areas of the printing plate during a press  
20 run. This is usually realized with acid, usually phosphoric acid, and gum arabic, the acid and gum combining to form a molecule that helps the adsorption of the gum to the metal of the plate and thereby making a hydrophilic surface.

WO 01/88958 discloses in claim 1 a method of forming a pattern  
25 of a functional material on a substrate comprising: applying a first pattern of a first material to said substrate; and applying a second functional material to said substrate and said first material, wherein said first material, said second functional material, and said substrate interact to spontaneously form a  
30 second pattern of said second functional material on said substrate, to thereby form a pattern of a functional material on a substrate.

WO 01/88958 further discloses in claim 27 a method of forming a pattern of a functional material on a substrate comprising: non-  
35 contact printing a first pattern of a first material on said substrate; and applying a second functional material to said substrate and said first material, wherein said first material, said second material, and said substrate interact to spontaneously form a second pattern of said second functional material on said  
40 substrate, to thereby form a pattern of a functional material on a substrate.



WO 01/88958 also discloses in claim 47 a method of forming a pattern of a functional material on a substrate comprising: non-contact printing a first pattern of a first material on said substrate; and applying a second functional material to said  
5 substrate and said first material, wherein said first and second functional materials are selected to have a sufficient difference in at least one property of hydrophobicity and hydrophilicity relative to one another such that said first material, said second functional material, and said substrate interact to spontaneously  
10 form a second pattern of said second functional material on said substrate, to thereby form on said substrate a second pattern of said second functional material, wherein said second pattern is the inverse of said first pattern, to thereby form a pattern of a functional material on a substrate.

15 WO 01/88958 also discloses in claim 57 a method of forming an electrical circuit element, comprising: applying a first pattern of a first material on a substrate; and applying a second material to said substrate and said first material, wherein said first material, said second material, and said substrate interact to  
20 spontaneously form a second pattern of said second material on said substrate, thereby forming an electrical circuit element.

WO 01/88958 also discloses in claim 110 an electrical circuit element comprising: a substrate; a first pattern of an insulating material applied to said substrate; and a second pattern of an  
25 electrically conducting material applied to said substrate and said first material, wherein said insulating material, said electrically conducting material, and said substrate interact to spontaneously form a second pattern of said electrically conducting material on said substrate when said electrically conducting material is  
30 applied to said substrate having said first pattern of said insulating material applied thereon.

WO 01/88958 also discloses in claim 123 an electronic device comprising: a) a first element comprising i) a first substrate; ii) a first pattern of an insulating material applied to said substrate  
35 and iii) a second pattern of an electrically conducting material applied to said substrate and said first material, wherein said insulating material, electrically conducting material, and said substrate interact to spontaneously form a second pattern of said electrically conducting material on said substrate when said  
40 electrically conducting material is applied to said substrate having said first pattern of said insulating material applied thereon; b) a second circuit element comprising i) a second

substrate; ii) a third pattern of an insulating material applied to said second substrate and iii) a fourth pattern of an electrically conducting material applied to said second substrate and said third material, wherein said insulating, electrically conducting material, and said second substrate interact to spontaneously form a fourth pattern of said electrically conducting material on said substrate when said electrically conducting material is applied to said substrate having said third pattern of said insulating material applied thereon; and c) an electrically connection between said first and second circuit elements.

WO 01/88958 also discloses in claim 127 a Radio Frequency (RF) tag comprising a pattern of a non-conductive first material on a substrate and a coating of an electrically conductive second material disposed over said substrate and said first material, wherein said first material, said second material, and said substrate interact to spontaneously form a second pattern of said second material on said substrate, to thereby form an Inductor-Capacitor (LC) resonator on said substrate.

WO 01/88958 also discloses in claim 141 a mechanical device comprising: a) a first component comprising: i) a first substrate; ii) a first pattern of first material to said first substrate and iii) a second pattern of material applied to said first substrate and said first material, wherein said second pattern of said second material is spontaneously formed by the interaction of said first material, said second material and said first substrate; and b) a second component comprising i) a second substrate; ii) a third pattern of a third material applied to said second substrate and iii) a fourth pattern of a fourth material applied to said second substrate and said third material, wherein said fourth pattern of said fourth material is spontaneously formed by the interaction of said third material, said fourth material and said substrate; and wherein said first and second components are oriented in a such a way that the second and fourth patterns oppose each other, and are selected from the group consisting of identical patterns, inverse patterns, and any mechanically useful combinations.

In 2001, Hohnholz et al. in Synthetic Metals, volume 121, pages 1327-1328, reported a novel method for the preparation of patterns from conducting and non-conducting polymers on plastic/paper substrates. This method, "Line Patterning" (LP), does not involve printing of the polymers and incorporates mostly standard office equipment, e.g. an office type laser printer. It

is rapid and inexpensive. The production of electronic components, e.g. a liquid crystal and a push-button assembly were reported.

It has been found that aqueous solutions and dispersions of intrinsically conductive polymers upon coating upon a surface with hydrophobic and hydrophilic areas eventually exclusively permeate to the hydrophilic areas, but at a speed which makes such processes industrially impracticable. There is a need for a mass-production process for producing conductive patterns of intrinsically conductive polymer.

10

Aspects of the invention

It is therefore an aspect of the present invention to provide a process for producing conductive patterns of intrinsically conductive polymers.

15

Further aspects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention

20

Surprisingly it has been found that if, in a conventional offset printing process using standard offset ink, the standard fountain is substituted by a fountain solution containing an intrinsically conductive polymer e.g. containing 3% by weight of poly(3,4-ethylenedioxythiophene) [PEDOT]/poly(styrene-sulfonate) [PSS], prints are immediately obtained with a conductive pattern in the non-inked areas corresponding to the hydrophilic areas of the offset printing plate used, which pattern is maintained in an extended printing run i.e. a stable situation is realized upon the offset printing plate with the hydrophobic areas being inked with the hydrophobic printing ink and the hydrophilic areas being wetted with the modified fountain solution. On the other hand, if no printing ink is used some surface resistance differentiation is observed in the first few prints corresponding to the hydrophilic pattern on the offset printing plate, but degree of surface resistance differentiation decreased with successive prints and had completely disappeared by the fifteenth print.

30

Aspects of the present invention have been realized by a process for the offset printing of conductive patterns comprising in any order the steps of: applying a printing ink to a printing plate and wetting the printing plate with an aqueous fountain

40

medium containing a solution or a dispersion of an intrinsically conductive polymer

Preferred embodiments are disclosed in the dependent claims.  
Detailed description of the invention

5

#### Definitions

The term alkoxy means all variants possible for each number of carbon atoms in the alkoxy group i.e. for three carbon atoms: n-  
10 propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

The term oxyalkylenealkoxy means two oxygen atoms linked by an alkylene group. An alkylene group is a substituted or  
15 unsubstituted hydrocarbon group e.g. a  $-(CH_2)_n-$  group where n is an integer between 1 and 5, which may be substituted with an alkoxy, aryloxy, alkyl, aryl, alkaryl, alkyloxyalkyl, alkyloxyalkaryl, alkyloxyaryl, hydroxy, carboxy, carboxyalkyl, carboxyamino, sulfo or alkylsulfo group.

20 The term derivatives as used in connection with a particular polymer refers to variants thereof substituted with alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulfonato and carboxy ester groups.

The term transparent layer as used in disclosing the present invention means permitting the passage of light in such a way that  
25 objects can be clearly seen through the layer.

The term aqueous medium means a medium containing water and water-miscible organic solvents containing between 50% by weight of water and 100% by weight of water.

The term layer according to the present invention means a  
30 continuous or discontinuous coating.

The term pattern according to the present invention means a discontinuous coating.

The term flexible as used in disclosing the present invention means capable of following the curvature of a curved object such as  
35 a drum e.g. without being damaged.

The term printing ink, according to the present invention, means an ink, which may or may not be pigmented with at least one dye or pigment and which is suitable for offset printing i.e. accepted by the oleophilic areas of a printing master plate,  
40 commonly known as a printing plate.

The term dye, according to the present invention, means a coloring agent having a solubility of 10 mg/L or more in the medium in which it is applied and under the ambient conditions pertaining.

The term pigment is defined in DIN 55943, herein incorporated  
5 by reference, as an inorganic or organic, chromatic or achromatic coloring agent that is practically insoluble in the application medium under the pertaining ambient conditions, hence having a solubility of less than 10 mg/L therein.

The term coated paper as used in disclosing the present  
10 invention is paper coated with any substance i.e. includes both clay-coated paper and resin-coated paper.

Freeze drying according to the present invention is a lyophilization process in which a substance is first frozen and then the quantity of solvent (generally water) is reduced, first by  
15 sublimation (=primary drying process) and then by desorption (=secondary drying process) until the temperature of the shelves becomes equal to the atmospheric temperature in the freeze dryer. The freeze-drying process is enabled by the ability of solid materials such as ice to sublime (change directly into a gas  
20 without passing through a liquid phase) under the right conditions.

The term "dry product" according to the present invention means dry to touch and is associated with no apparent liquid phase.

The term conductive means having a surface resistance or  $10^{11}$   $\Omega$ /square or less and is a generic term including both the terms  
25 antistatic and electroconductive. The term electroconductive means having a surface resistance below  $10^6$   $\Omega$ /square. Antistatic materials have surface resistances in the range from  $10^6$  to  $10^{11}$   $\Omega$ /square and cannot be used as an electrode.

The electric resistance of a layer is generally expressed in  
30 terms of surface resistance  $R_s$  (unit  $\Omega$ ; often specified as  $\Omega$ /square). Alternatively, it may be expressed in terms of volume resistivity  $R_v = R_s \cdot d$ , wherein  $d$  is the thickness of the layer, volume conductivity  $k_v = 1/R_v$  [unit: S(iemens)/cm] or surface conductance  $k_s = 1/R_s$  [unit: S(iemens).square].

35 Conductivity enhancement refers to a process in which contact with high boiling point liquids such as di- or polyhydroxy- and/or carboxy groups or amide or lactam group containing organic compound optionally followed by heating at elevated temperature, preferably between 100 and 250 °C, during preferably 1 to 90 seconds, results  
40 in conductivity increase. Alternatively in the case of aprotic compounds with a dielectric constant  $\geq 15$ , e.g. N-methyl-pyrrolidinone, temperatures below 100°C can be used. Such

conductivity enhancement is observed with polythiophenes and can take place during the preparation of a layer or subsequently. Particularly preferred liquids for such treatment are N-methyl-pyrrolidinone and diethylene glycol such as disclosed in EP-A 686 662 and EP-A 1 003 179, herein incorporated by reference.

PEDOT as used in the present disclosure represents poly(3,4-ethylenedioxythiophene).

PSS as used in the present disclosure represents poly(styrene sulphonic acid) or poly(styrenesulphonate).

PET as used in the present disclosure represents poly(ethylene terephthalate).

The term improved in referring to aqueous dispersions of PEDOT/PSS refers to aqueous dispersions of PEDOT/PSS prepared according to the polymerization process disclosed in EP-A 0 440 957 except that the polymerization process is carried out in the substantial absence of oxygen.

#### Aqueous fountain medium

Aspects of the present invention have been realized by a process for the offset printing of patterns of intrinsically conductive polymers, characterized in that the fountain contains an aqueous solution or dispersion of an intrinsically conductive polymer.

The intrinsically conductive polymer may be incorporated into the aqueous fountain medium as a conventional aqueous dispersion of an intrinsically conductive polymer, such as available using the process disclosed in EP-A 0 440 957, as a product obtained by simple evaporation thereof or as a freeze-dried dry-to-touch product obtained by freeze-drying thereof as disclosed in WO 02/00759. Alternatively improved aqueous dispersions of an intrinsically conductive polymers can be used, such as obtained by polymerizing intrinsically conductive polymers in the substantial absence of oxygen.

The fountain solutions may also contain: water-soluble gums, a pH buffer system, desensitizing salts, acids or their salts, wetting agents, solvents, non-piling or lubricating additives, emulsion control agents, viscosity builders, biocides, defoamers and dyes.

According to a first embodiment of the process, according to the present invention, the aqueous fountain medium further contains

an anti-foaming agent. Suitable anti-foaming agents include the silicone antifoam agent X50860A from Shin-Etsu.

According to a second embodiment of the process, according to the present invention, the aqueous fountain medium has a viscosity  
5 at 25°C after stirring to constant viscosity of at least 30 mPa.s as measured according to DIN 53211 i.e. until successive measurements according to DIN 53211 are reproducible.

According to a third embodiment of the process, according to the present invention, the aqueous fountain medium has a viscosity  
10 at 25°C after stirring to constant viscosity of at least 100 mPa.s as measured according to DIN 53211 i.e. until successive measurements according to DIN 53211 are reproducible.

According to a fourth embodiment of the process, according to the present invention, the aqueous fountain medium has a viscosity  
15 at 25°C after stirring to constant viscosity of at least 200 mPa.s as measured according to DIN 53211 i.e. until successive measurements according to DIN 53211 are reproducible.

According to a fifth embodiment of the process, according to the present invention, the aqueous fountain medium has a pH between  
20 1.5 and 5.5.

According to a sixth embodiment of the process, according to the present invention, the aqueous fountain medium further contains a water-soluble gum, such as gum arabic, larch gum, CMC, PVP, and acrylics.

25

#### Intrinsically conductive polymer

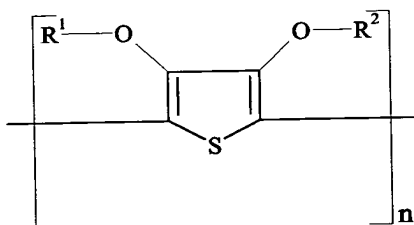
According to a seventh embodiment of the process, according to the present invention, the intrinsically conductive polymer is  
30 selected from the group consisting of polyanilines, polyaniline derivatives, polypyrroles, polypyrrole derivatives, polythiophenes and polythiophene derivatives.

According to an eighth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a  
35 polymer or copolymer of a 3,4-dialkoxythiophene in which the two alkoxy groups may be the same or different or together represent an oxy-alkylene-oxy bridge optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulphonato and carboxy ester groups.

40 According to a ninth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxythiophene in which the two

alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge which is a 1,2-ethylene group, an optionally alkyl-substituted methylene group, an optionally C<sub>1-12</sub>-alkyl- or phenyl-substituted 1,2-ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group, the substituents for the oxy-alkylene-oxy bridge being selected from the group consisting of alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulphonato and carboxy ester groups.

According to a tenth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a (3,4-dialkoxythiophene) has the formula



in which, each of R<sup>1</sup> and R<sup>2</sup> independently represents hydrogen or a C<sub>1-5</sub>-alkyl group or together represent a C<sub>1-5</sub> alkylene group or a cycloalkylene group optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulphonato and carboxy ester groups.

According to an eleventh embodiment of the process, according to the present invention, the intrinsically conductive polymer is selected from the group consisting of: homopolymers of (3,4-methylenedioxy-thiophene), (3,4-methylenedioxythiophene) derivatives, (3,4-ethylenedioxythiophene), (3,4-ethylenedioxythiophene) derivatives, (3,4-propylenedioxythiophene), (3,4-(propylenedioxythiophene) derivatives, (3,4-butylenedioxythiophene) and (3,4-butylenedioxythiophene) derivatives and copolymers thereof.

Such polymers are disclosed in Handbook of Oligo- and Polythiophenes Edited by D. Fichou, Wiley-VCH, Weinheim (1999); by L. Groenendaal et al. in Advanced Materials, volume 12, pages 481-494 (2000); L. J. Kloeppner et al. in Polymer Preprints, volume 40(2), page 792 (1999); P. Schottland et al. in Synthetic Metals, volume 101, pages 7-8 (1999); and D. M. Welsh et al. in Polymer Preprints, volume 38(2), page 320 (1997).

#### Polyanion

According to a twelfth embodiment of the process, according to the present invention, the aqueous fountain medium further contains



a polyanion. Suitable polyanions include the polyanions of polymeric carboxylic acids, e.g. polyacrylic acids, polymethacrylic acids, or polymaleic acids, and polysulphonic acids, e.g. poly(styrene sulphononic acid). These polycarboxylic acids and  
5 polysulphonic acids can also be copolymers of vinylcarboxylic acids and vinylsulphonic acids with other polymerizable monomers, e.g. acrylic acid esters, methacrylic acid esters and styrene.

According to a thirteenth embodiment of the process, according to the present invention, the fountain medium further contains a  
10 poly(styrenesulfonate) polyanion or a polyanion of a copolymer of polystyrenesulphonic acid with styrene.

According to a fourteenth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxythiophene, fountain medium  
15 further contains a polyanion and the molar ratio of the polymer or copolymer of a 3,4-dialkoxythiophene to polyanion is in the range of 1:0.95 to 1:6.5.

According to a fifteenth embodiment of the process, according to the present invention, the intrinsically conductive polymer is a  
20 polymer or copolymer of a 3,4-dialkoxythiophene, fountain medium further contains a polyanion and the molar ratio of the polymer or copolymer of a 3,4-dialkoxythiophene to polyanion is in the range of 1:0.95 to 1:3.0.

#### 25 Water-miscible organic compound

According to a sixteenth embodiment of the process, according to the present invention, the aqueous fountain medium further contains at least one water-miscible organic compound, such as  
30 aliphatic alcohols, ketones, arenes, esters, glycol ethers, cyclic ethers, such as tetrahydrofuran, and their mixtures.

According to a seventeenth embodiment of the process, according to the present invention, the aqueous fountain medium further contains at least one high boiling point liquid such as di-  
35 or polyhydroxy- and/or carboxy groups or amide or lactam group containing organic compounds capable of producing conductivity enhancement, e.g. by heating at elevated temperature, preferably between 100 and 250 °C, during 1 to 90 seconds, such as diethylene glycol, 1,2-propandiol, glycerol, hexylene glycol, propylene  
40 glycol, di(ethylene glycol)ethyl ether acetate (carbitol® acetate), N-methylacetamide, N-methyl pyrrolidinone (NMP) and sugar alcohols, such as sorbitol, mannitol, saccharose and fructose.

According to an eighteenth embodiment of the process, according to the present invention, the aqueous fountain medium further contains at least one aprotic compound with a dielectric constant  $\geq 15$  capable of producing conductivity enhancement at  
5 temperatures below 100°C, such as N-methyl-pyrrolidinone (NMP), 2-pyrrolidinone, 1,3-dimethyl-2-imidazolidone, N,N,N',N'-tetramethylurea, formamide, N,N-dimethylformamide, N,N-dimethylacetamide, tetramethylene sulphone, dimethyl sulphoxide and hexamethylphosphoramide.

10 According to a nineteenth embodiment of the process, according to the present invention, the aqueous fountain medium further contains at least one water-miscible organic compound selected from the group consisting of 1,2-propandiol, propylene glycol, diethylene glycol, N-methyl pyrrolidinone and di(ethylene  
15 glycol)ethyl ether acetate (carbitol® acetate).

The suitability of particular organic solvents can be evaluated by mixing 8g of a 1.2% by weight aqueous dispersion of PEDOT/PSS with 12g of solvent. If miscibility is observed without gel formation, the non-aqueous solvent is regarded as suitable.  
20 Tetrahydrofuran is miscible, but the dispersions are very viscous. Suitability according to the above miscibility test does not rule out phase separation upon further dilution of the PEDOT/PSS-dispersion with the same solvent, as is observed with tetrahydrofuran. It will be understood by one skilled in the art  
25 that a PEDOT/PSS-dispersion cannot be diluted to an unlimited extent without the possibility of phase separation. Ethyl lactate induces gel-formation and hence is unsuitable. Benzyl alcohol, furfuryl alcohol and cyclohexane produced phase separation and hence are unsuitable.

30 According to a twentieth embodiment of the process, according to the present invention, the aqueous fountain medium further contains a di- or polyhydroxy- and/or carboxy groups or amide or lactam group containing organic compound and the process further contains a step subsequent to printing in which said receiving  
35 medium within 10 minutes of printing is heated to a temperature of 100 to 250°C.

According to a twenty-first embodiment of the process, according to the present invention, the aqueous fountain medium further contains an aprotic organic compound with a dielectric  
40 constant  $\geq 15$  and the process further contains a step subsequent to printing in which the receiving medium within 10 minutes of printing is heated to a temperature of  $\leq 150^\circ\text{C}$ .

According to a twenty-second embodiment of the process, according to the present invention, the process further contains a obtaining a print by printing on a receiving medium, applying a liquid comprising a di- or polyhydroxy- and/or carboxy groups or  
 5 amide or lactam group containing organic compound to the print, and heating the print after application of the liquid to a temperature of 100 to 250°C.

According to a twenty-third embodiment of the process, according to the present invention, the process further contains a  
 10 obtaining a print by printing on a receiving medium, applying a liquid comprising an aprotic organic compound with a dielectric constant  $\geq 15$  to the print, and heating the print after application of the liquid to a temperature of  $\leq 150^\circ\text{C}$ .

15

#### Pigments and dyes

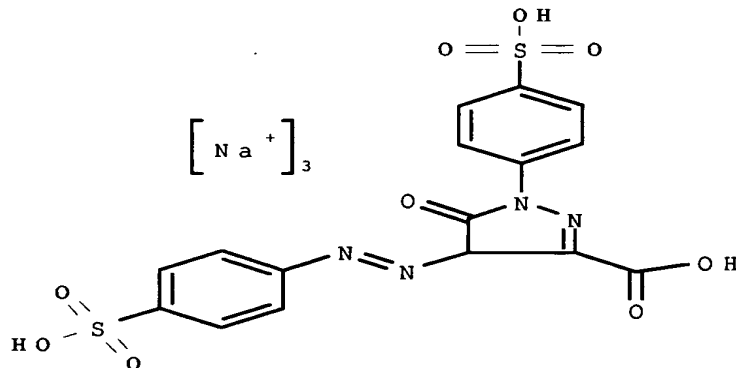
According to a twenty-fourth embodiment of the process, according to the present invention, the aqueous fountain medium further contains a pigment.

20 Transparent coloured compositions can be realized by incorporating pigments e.g. azo pigments e.g. DALMAR® Azo Yellow and LEVANYL® Yellow HRLF, dioxazine pigments e.g. LEVANYL® Violet BNZ, phthalocyanine blue pigments, phthalocyanine green pigments, Molybdate Orange pigments, Chrome Yellow pigments, Quinacridone  
 25 pigments, Barium precipitated Permanent Red 2B, manganese precipitated BON Red, Rhodamine B pigments and Rhodamine Y pigments.

According to a twenty-fifth embodiment of the process, according to the present invention, the aqueous fountain medium  
 30 further contains a dye.

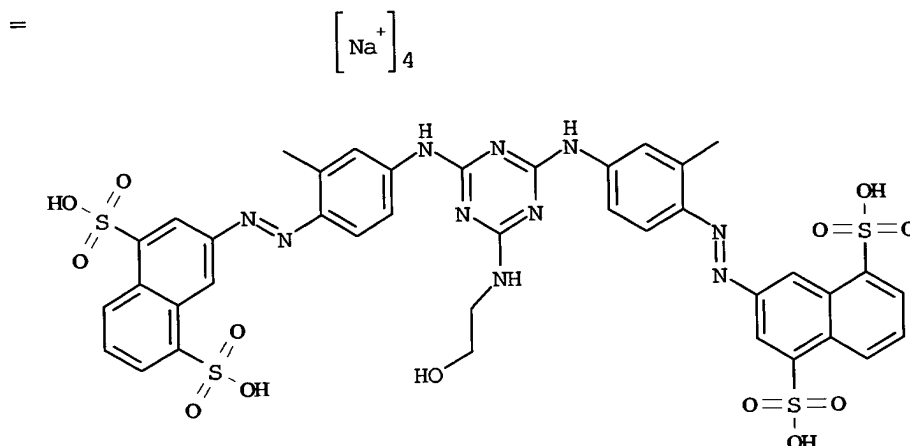
Suitable dyes include:

Acid Yellow =  
 23 (Tartra-  
 phenine)  
 (from  
 Clariant,  
 Germany)

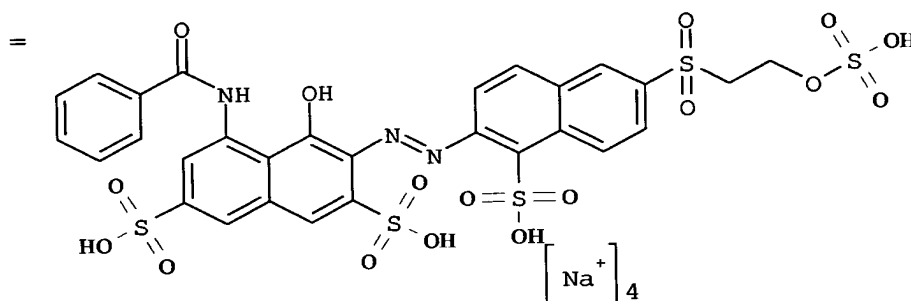


14

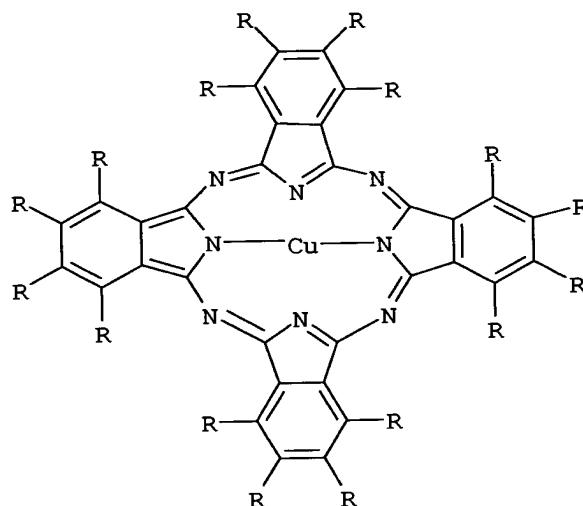
Direct  
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(from  
Farbenchem,  
Germany)



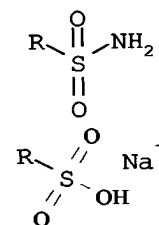
Reactive  
Red 180  
(from  
Aakash,  
USA)



Direct Blue  
199 (from  
Farbenchem,  
Germany)



R



According to a twenty-sixth embodiment of the process, according to the present invention, the aqueous fountain medium further contains a dye and/or a pigment such that the colour tone of the ink and the background cannot be distinguished by the human eye e.g. by colour matching or colour masking by for example matching the CIELAB  $a^*$ ,  $b^*$  and  $L^*$  values as defined in ASTM Norm E179-90 in a R(45/0) geometry with evaluation according to ASTM Norm E308-90.

According to a twenty-seventh embodiment of the process, according to the present invention, the printing ink further contains a dye and/or a pigment such that the colour tone of the ink and the background cannot be distinguished by the human eye  
5 e.g. by colour matching or colour masking by for example matching the CIELAB a\*, b\* and L\* values as defined in ASTM Norm E179-90 in a R(45/0) geometry with evaluation according to ASTM Norm E308-90.

### Surfactants

10

According to a twenty-eighth embodiment of the process, according to the present invention, the aqueous fountain medium further contains a surfactant.

According to a twenty-ninth embodiment of the process,  
15 according to the present invention, the aqueous fountain medium further contains a non-ionic surfactant e.g. ethoxylated/fluororalkyl surfactants, polyethoxylated silicone surfactants, polysiloxane/polyether surfactants, ammonium salts of perfluoro-alkylcarboxylic acids, polyethoxylated surfactants and  
20 fluorine-containing surfactants.

Suitable non-ionic surfactants include:

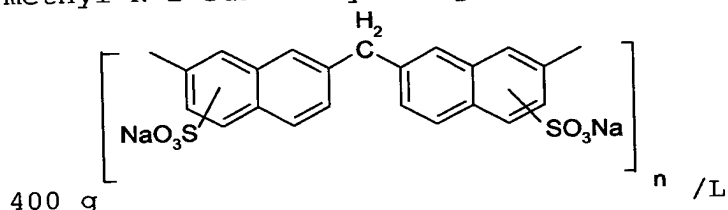
- |                          |  |
|--------------------------|--|
| NON01 SURFYNOL® 440:     | an acetylene compound with two polyethylene oxide chains having 40wt% of polyethylene oxide groups from Air Products                             |
| NON02 SYNPERONIC®13/6.55 | a tridecylpolyethylene-glycol  |
| NON03 ZONYL® FSO-100:    | a mixture of ethoxylated fluoro-surfactants with the formula:<br>$F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_yH$ where $y = 0$ to ca. 15 from DuPont; |
| NON04 ARKOPAL™ N060:     | a nonylphenylpolyethylene-glycol from HOECHST  |
| NON05 FLUORAD® FC129:    | a fluoroaliphatic polymeric ester from 3M  |
| NON06 PLURONIC® L35      | a polyethylene-glycol/propylene-glycol   |
| NON07 TEGOGLIDE® 410:    | a polysiloxane-polymer copolymer surfactant, from Goldschmidt;   |
| NON08 TEGOWET®:          | a polysiloxane-polyester copolymer surfactant, from Goldschmidt;   |
| NON09 FLUORAD® FC126:    | a mixture of ammonium salts of perfluorocarboxylic acids, from 3M;   |
| NON10 FLUORAD® FC430:    | a 98.5% active fluoroaliphatic ester from  |

- NON11 FLUORAD® FC431: 3M;  
 $\text{CF}_3(\text{CF}_2)_7\text{SO}_2(\text{C}_2\text{H}_5)\text{N}-\text{CH}_2\text{CO}-(\text{OCH}_2\text{CH}_2)_n\text{OH}$  from 3M;
- NON12 Polyoxyethylene-10-lauryl ether
- NON13 ZONYL® FSN: a 40% by weight solution of  
 $\text{F}(\text{CF}_2\text{CF}_2)_{1-9}\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$  in a 50% by weight solution of isopropanol in water where  $x = 0$  to about 25, from DuPont;
- NON14 ZONYL® FSN-100:  $\text{F}(\text{CF}_2\text{CF}_2)_{1-9}\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$  where  $x = 0$  to about 25, from DuPont;
- NON15 ZONYL® FS300: a 40% by weight aqueous solution of a fluorinated surfactant, from DuPont;
- NON16 ZONYL® FSO: a 50% by weight solution of a mixture of ethoxylated fluoro-surfactants with the formula:  $\text{F}(\text{CF}_2\text{CF}_2)_{1-7}\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{H}$  where  $y = 0$  to ca. 15 in a 50% by weight solution of ethylene glycol in water, from DuPont;

According to a thirtieth embodiment of the process, according to the present invention, the aqueous fountain medium further contains an anionic surfactant. Suitable anionic surfactants include:

- AN01 HOSTAPON® T a 95% concentrate of purified sodium salt of N-methyl-N-2-sulfoethyl-oleylamide, from HOECHST

AN02 LOMAR® D



- AN03 AEROSOL® OT an aqueous solution of 10g/L of the sodium salt of the di-2-ethylhexyl ester of sulphosuccinic acid from American Cyanamid
- AN04 DOWFAX 2A1 a 45% by weight aqueous solution of a mixture of the sodium salt of bis (p-dodecyl,sulpho-phenyl)-ether and the sodium salt of (p-dodecyl,sulpho-phenyl)(sulpho-phenyl)ether from Dow Corning
- AN05 SPREMI tetraethylammonium perfluoro-octylsulphonate
- AN06 TERGO sodium 1-isobutyl,4-ethyl-n-octylsulphate
- AN07 ZONYL® 7950 a fluorinated surfactant, from DuPont;
- AN08 ZONYL® FSA a 25% by weight solution of

- F(CF<sub>2</sub>CF<sub>2</sub>)<sub>1-9</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>COOLi in a 50% by weight solution of isopropanol in water, from DuPont;
- AN09 ZONYL® FSE: 14% by weight solution of  
 [F(CF<sub>2</sub>CF<sub>2</sub>)<sub>1-7</sub>CH<sub>2</sub>CH<sub>2</sub>O]<sub>x</sub>P(O)(ONH<sub>4</sub>)<sub>y</sub> where x = 1 or 2; y = 2 or 1; and x + y = 3 in a 70% by weight solution of ethylene glycol in water, from DuPont;
- AN10 ZONYL® FSJ: 40% by weight solution of a blend of  
 F(CF<sub>2</sub>CF<sub>2</sub>)<sub>1-7</sub>CH<sub>2</sub>CH<sub>2</sub>O]<sub>x</sub>P(O)(ONH<sub>4</sub>)<sub>y</sub> where x = 1 or 2; y = 2 or 1; and x + y = 3 with a hydrocarbon surfactant in 25% by weight solution of isopropanol in water, from DuPont;
- AN11 ZONYL® FSP 35% by weight solution of  
 [F(CF<sub>2</sub>CF<sub>2</sub>)<sub>1-7</sub>CH<sub>2</sub>CH<sub>2</sub>O]<sub>x</sub>P(O)(ONH<sub>4</sub>)<sub>y</sub> where x = 1 or 2; y = 2 or 1 and x + y = 3 in 69.2% by weight solution of isopropanol in water, from DuPont;
- AN12 ZONYL® UR: [F(CF<sub>2</sub>CF<sub>2</sub>)<sub>1-7</sub>CH<sub>2</sub>CH<sub>2</sub>O]<sub>x</sub>P(O)(OH)<sub>y</sub> where x = 1 or 2; y = 2 or 1 and x + y = 3, from DuPont;
- AN13 ZONYL® TBS: 33% by weight solution of F(CF<sub>2</sub>CF<sub>2</sub>)<sub>3-8</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H in a 4.5% by weight solution of acetic acid in water, from DuPont;
- AN14 ammonium salt of perfluoro-octanoic acid.

According to a thirty-first embodiment of the process, according to the present invention, the aqueous fountain medium further contains an amphoteric surfactant. Suitable amphoteric  
 5 surfactants include:

AMP01 AMBITERIC® H a 20% by weight solution of hexadecyldimethyl-ammonium acetic acid in ethanol

#### Preparation process for the aqueous fountain medium

10 According to a thirty-second embodiment of the process, according to the present invention, the process further includes a process for preparing the aqueous fountain medium.

The process for preparing the aqueous fountain medium used in the process, according to the present invention, uses an  
 15 intrinsically conductive polymer in a state dry to the touch or as an aqueous solution or dispersion. If in a state dry to the touch, the intrinsically conductive polymer must be readily dispersible or soluble in an aqueous medium. An example of a dry to the touch intrinsically conductive polymer which is readily dispersible in an

aqueous medium is obtainable by freeze drying an aqueous dispersion of a latex comprising a polyanion and a polymer or copolymer of a substituted or unsubstituted thiophene as disclosed in WO 02/00759, herein incorporated by reference. Alternatively a solution or  
5 dispersion of an intrinsically conductive polymer in an aqueous medium can simply be evaporated as, for example, disclosed in WO 99/34371.

According to a thirty-third embodiment of the process, according to the present invention, the process further contains a  
10 process for preparing the aqueous fountain medium using an intrinsically conductive polymer obtained by freeze drying an aqueous dispersion of a latex comprising a polyanion and a polymer or copolymer of a substituted or unsubstituted thiophene.

#### 15 Receiving medium

According to a thirty-fourth embodiment of the process, according to the present invention, is any medium receiving medium suitable for offset printing.

20 According to a thirty-fifth embodiment of the process, according to the present invention, the receiving medium is paper, coated paper, a metallic foil or a plastic sheet.

The receiving medium may be translucent, transparent or opaque. Suitable plastic sheets include a polymer laminate, a  
25 thermoplastic polymer foil or a duroplastic polymer foil e.g. made of a cellulose ester, cellulose triacetate, polypropylene, polycarbonate or polyester, with poly(ethylene terephthalate) or poly(ethylene naphthalene-1,4-dicarboxylate) being particularly preferred.

30

#### Industrial application

The process according to the present invention can, for example, be used to produce conductive patterns for a multiplicity  
35 of applications including electroplating with metallic layers, the production of electrical circuitry for single and limited use items such as toys, in capacitive antennae as part of radiofrequency tags, in electroluminescent devices which can be used in lamps, displays, back-lights e.g. LCD, automobile dashboard and keyswitch  
40 backlighting, emergency lighting, cellular phones, personal digital assistants, home electronics, indicator lamps and other applications in which light emission is required.



The invention is illustrated hereinafter by way of COMPARATIVE EXAMPLES and INVENTION EXAMPLES. The percentages and ratios given in these examples are by weight unless otherwise indicated.

5

The following receiving media were used in the COMPARATIVE and INVENTION EXAMPLES:

receiving medium nr	
1	RC-paper GN 279 from Schoeller a 110g/m <sup>2</sup> paper coated either side with a layer containing 19 g polyethylene/m <sup>2</sup> on one side and a layer containing 19 g polyethylene/m <sup>2</sup> and TiO <sub>2</sub> on the other side (side used for printing)
2	coated paper: ALLEGRO® GLOSS (115g/m <sup>2</sup> )
3	175µm thick PET with a subbing layer No. 01

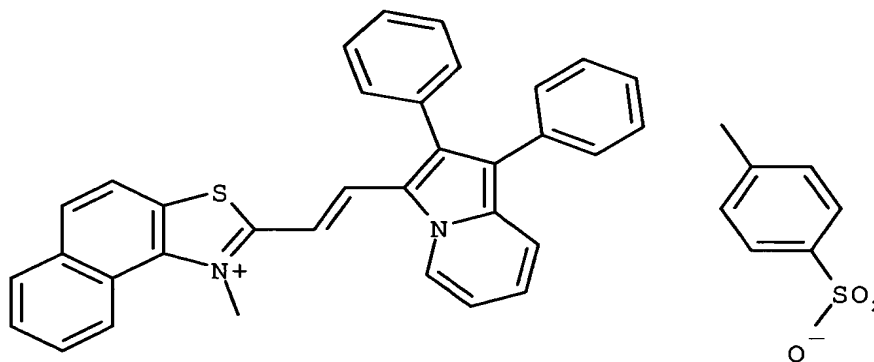
10 Subbing layer Nr. 01 has the composition:

copolymer of 88% vinylidene chloride, 10% methyl acrylate and 2% itaconic acid	79.1%
Kieselcol® 100F, a colloidal silica from BAYER	18.6%
Mersolat® H, a surfactant from BAYER	0.4%
Ultravon® W, a surfactant from CIBA-GEIGY	1.9%

Ingredients used in the COMPARATIVE and INVENTION EXAMPLES:

- IR-absorbing dyes:

15 IR01 =



Aqueous PEDOT/PSS dispersions used in the COMPARATIVE and INVENTION EXAMPLES

20

A 1.2% by weight aqueous dispersion of PEDOT/PSS containing a weight ratio PEDOT to PSS of 1:2.4 was prepared as disclosed in EP-A 440 957 and had a typical viscosity measured using an AR1000 plate and cone rheometer (diameter 4 cm; cone angle 2°) at 20°C of 38 mPa.s at a shear rate of 5 s<sup>-1</sup> decreasing to 33.5 mPa.s at a shear rate of 35 s<sup>-1</sup> and has a typical pH of 1.9. A 3% by weight dispersion of PEDOT/PSS was then prepared from this 1.2% by weight dispersion by evaporating 60.7% by weight of the water with stirring at a temperature of 75°C and a pressure of 50 mbar.

10

Printing plates used in the COMPARATIVE and INVENTION EXAMPLES

Printing plates 1 and 2 were prepared by doctor-blade coating a 175 µm subbed PET support to a wet layer thickness of 40 µm with the following compositions:

	Printing plate 1	Printing plate 2
poly(tetrahydropyran-2-yl methacrylate)	0.90 g	-
copolymer of tetrahydropyran-2-yl methacrylate & methyl methacrylate	-	0.90 g
IR01, an IR-absorbing dye	0.10 g	0.10 g
TEGOGLIDE™ 410 (2% solution)	0.03 g	0.03 g
2-butanone	14.97 g	14.97 g
Total	16.0 g	16.0 g

giving ingredient coverages of:

	Printing plate 1	Printing plate 2
poly(tetrahydropyran-2-yl methacrylate)	1.80 g/m <sup>2</sup>	-
copolymer of tetrahydropyran-2-yl methacrylate & methyl methacrylate	-	1.80 g/m <sup>2</sup>
IR01, an IR-absorbing dye	0.20 g/m <sup>2</sup>	0.20 g/m <sup>2</sup>
TEGOGLIDE™ 410 (2% solution)	0.0012 g/m <sup>2</sup>	0.0012 g/m <sup>2</sup>

20

Printing plates 3 and 4 are commercially available from AGFA-GEVAERT N.V.:

- Printing plate 3: THERMOSTAR™ P970/15
- Printing plate 4: SETPRINT™ SET/R

25

Aqueous fountain media

Six aqueous fountain media were used in the INVENTION EXAMPLES:

Aqueous fountain medium	
AFM-01	1.2% aqueous PEDOT/PSS dispersion
AFM-02	aqueous dispersion with 1.2% PEDOT/PSS and 5.0% NMP
AFM-03	3.0% aqueous PEDOT/PSS dispersion
AFM-04	aqueous dispersion with 2.8% PEDOT/PSS and 7.5% NMP
AFM-05	aqueous dispersion with 2.8% PEDOT/PSS and 15% NMP
AFM-06	aqueous dispersion with 2.8% "improved" PEDOT/PSS and 7.5% NMP

5 and two in the COMPARATIVE EXAMPLES:

Aqueous fountain medium	
AFM-C01	G671C fountain solution from AGFA-GEVAERT, an aqueous solution containing 5% isopropanol
AFM-C02	3.0% aqueous solution of poly(styrenesulphonic acid)

COMPARATIVE EXAMPLES 1 and INVENTION EXAMPLES 1 to 3

10 Printing experiments were carried out with a 360 offset printer from A.B. Dick with NOVAQUICK™ schwarz 123W, a black offset ink from BASF, using printing plates, aqueous fountain media and receiving media given in Table 1 below.

In COMPARATIVE EXAMPLE 1 a standard aqueous fountain medium, 15 AFM-C01, was used with printing plate nr. 4, NOVAQUICK™ schwarz 123W being used as the printing ink.

In INVENTION EXAMPLES 1 to 3, aqueous fountain medium AFM-02, a 3% by weight dispersion of PEDOT/PSS, was used as the aqueous fountain medium with printing plates 1, 2 and 3 respectively.

20 For each example, the aqueous fountain medium was deposited on the fountain roll and the NOVAQUICK™ schwarz 123W printing ink was deposited on the ink roll with the aqueous fountain being applied to the printing plate before the printing ink. Printing was started after 10 revolutions of the fountain roll and 5 revolutions 25 of the ink roll. 30 sheets of the receiving medium were printed in each case and the surface resistances of the "inked" and "non-inked" areas measured with a two point method using a "Surface

Resistance Checker" from DALCON DULLAERT (ESD CONTROL). The surface resistances of the inked and non-inked areas are also given in Table 1.

5 Table 1:

Comparative Example nr	Printing plate nr.	Aqueous fountain medium nr.	receiving medium nr.	Surface resistance of inked area [ $\Omega$ /square]	Surface resistance of non-inked areas [ $\Omega$ /square]
1	4	AFM-C01	1	$10^{11}$	$10^{11}$
Invention Example nr.					
1	1	AFM-03	1	$10^{11}$	$10^9$
2	2	AFM-03	1	$10^{11}$	$10^9$
3	3	AFM-03	1	$10^{10}$	$10^8$

The surface resistances of the inked and inked areas of prints obtained in INVENTION EXAMPLE 3 were monitored as a function of the number of the print and for each print the evolution of the surface resistance values monitored under different conditions as a function of time. The results are given in Table 2 for prints stored in the dark.

15 Table 2:

time after printing	surface resistance of print 1 [ $\Omega$ /square]		surface resistance of print 5 [ $\Omega$ /square]		surface resistance of print 10 [ $\Omega$ /square]		surface resistance of print 20 [ $\Omega$ /square]		surface resistance of print 30 [ $\Omega$ /square]	
	non-inked areas	inked area	non-inked areas	inked area	non-inked areas	inked area	non-inked areas	inked area	non-inked areas	inked area
1 h			$10^8$	$10^{11}$					$10^8$	$10^{10}$
3 h									$10^8$	$10^{12}$
5 h	$10^9$	$10^{10}$			$10^8$	$10^{12}$	$10^8$	$10^{11}$	$10^8$	$10^{12}$
6 h	$10^8$	$10^{11}$			$10^8$	$10^{11}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$
3 days	$10^8$	$10^{11}$	$10^{8*}$	$10^{11*}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$
4 days	$10^8$	$10^{11}$			$10^8$	$10^{10}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$
5 days	$10^8$	$10^{11}$			$10^8$	$10^{11}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$
7 days	$10^8$	$10^{11}$			$10^8$	$10^{11}$	$10^8$	$10^{11}$	$10^8$	$10^{11}$

\* no change in surface resistance upon additional 15 minutes UV-exposure to a 1200 W halogen lamp with an intensity of  $40 \text{ W/m}^2$

The results in Table 2 show that the differentiation in surface resistance between the "inked" and "non-inked" areas in the dark increase with time and is unaffected by UV-exposure.

Table 3 shows the evolution in the surface resistances of the "inked" and "non-inked" areas with time upon exposure to direct and non-direct sunlight for prints produced in INVENTION EXAMPLE 3.

Table 3:

time after printing	Surface resistance of print 6 upon exposure to direct sunlight		Surface resistance of print 25 upon exposure to non-direct sunlight	
	non-inked areas	inked area	non-inked areas	inked area
1h	$10^8$	$10^{11}$	$10^8$	$10^{11}$
2 days	$10^8$	$10^{11}$	$10^8$	$10^{11}$
3 days	$10^9$	$10^{11}$	$10^8$	$10^{11}$
4 days	$10^9$	$10^{12}$	$10^8$	$10^{11}$
5 days	-	-	$10^8$	$10^{11}$
7 days	-	-	$10^9$	$10^{12}$

The differentiation in surface resistance between the "inked" and "non-inked" areas does not change with time upon exposure to direct or non-direct sunlight, although after 3 days exposure to direct sunlight the surface resistance of the inked areas increased from  $10^8 \text{ } \Omega/\text{square}$  to  $10^9 \text{ } \Omega/\text{square}$ .

#### INVENTION EXAMPLES 4 to 19 and COMPARATIVE EXAMPLES 2 to 6

INVENTION EXAMPLES 4 to 19 and COMPARATIVE EXAMPLES 2 to 6 were carried out as described for INVENTION EXAMPLES 1 to 3 and COMPARATIVE EXAMPLE 1 except that the printing ink used was NOVAVIT™ gelb 1 F 713, a yellow offset ink from BASF, printing plate nr. 3 was used, receiving medium used were types 1 to 3 and the aqueous fountain media AFM01 to AFM06 and AFM-C01 and AFM-C02 were used as specified for INVENTION EXAMPLES 4 to 19 and for COMPARATIVE EXAMPLES 2 to 6 in Table 4.

30 sheets of the receiving medium were printed in each case and the surface resistances of the "inked" and "non-inked" areas measured with a two point method as described for INVENTION EXAMPLES 1 to 3 and COMPARATIVE EXAMPLE 1. The surface resistances of the inked and non-inked areas are also given in Table 4.

Table 4:

Comparative Example nr	Aqueous fountain medium nr.	receiving medium nr.	Surface resistance of inked area [ $\Omega$ /square]		Surface resistance of non-inked areas [ $\Omega$ /square]	
			without heating	+ immediate heating for 10min/110°C	without heating	+ immediate heating for 10min/110°C
2	AFM-C01	1	$10^{12}$	—	$10^{12}$	—
3	AFM-C01	2	$10^{12}$	—	$10^{12}$	—
4	AFM-C02	1	$10^{10}$	$10^{11}$	$10^{10}$	$10^{11}$
5	AFM-C02	2	$10^{10}$	$10^{11}$	$10^{10}$	$10^{11}$
6	AFM-C02	3	$10^{11}$	$10^{12}$	$10^{11}$	$10^{12}$
Invention Example nr.						
4	AFM-01	1	$10^{12}$	—	$10^{11}$	—
5	AFM-01	2	$10^{12}$	—	$10^{11}$	—
6	AFM-02	1	$10^{12}$	—	$10^{12}$	—
7	AFM-02	2	$10^{12}$	—	$10^{11}$	—
8	AFM-03	1	$10^{10}$	—	$10^8$	—
9	AFM-03	2	$10^{10}$	—	$10^8$	—
10	AFM-04	1	$10^{11}$	$10^{12}$	$10^8$	$10^{11}$
11	AFM-04	2	$10^{11}$	$10^{11}$	$10^8$	$10^8$
12	AFM-04	3	$10^{11}$	$10^{12}$	$10^8$	$10^8$
13	AFM-05	1	$10^{12}$	$10^{12}$	$10^{12}$	$10^{12}$
14	AFM-05	2	$10^{11}$	$10^{11}$	$10^8$	$10^7$
15	AFM-05	2	$10^9$	—	$10^7$	—
16	AFM-05	2 twice*	$10^9$	—	$10^6$	—
17	AFM-05	3	$10^{10}$	$10^{11}$	$10^7$	$10^7$
18	AFM-06	1	$10^{11}$	$10^{10}$	$10^{10}$	$10^9$
19	AFM-06	2	$10^{10}$	$10^{11}$	$10^7$	$10^7$
19	AFM-06	3	$10^{11}$	$10^{11}$	$10^8$	$10^7$

\* two passes

Little conductivity enhancement was observed with aqueous fountain medium containing NMP upon immediately heating for 10 minutes at 110°C. However, that enhancement with NMP is feasible was shown by dipping the prints of INVENTION EXAMPLES 11 in NMP for 20s and then heating for 20 minutes at 110°C, which resulted in a thousand-fold reduction of the surface resistance in the non-printed areas from  $10^8$  to  $10^5$  ohm/square i.e. an increase in the ratio of surface resistance of the printed area to that of the non-printed area from  $10^3$  to  $10^6$ . Further heating experiments showed that, by varying the temperature and heating time immediately after printing for the prints of INVENTION EXAMPLE 15 with a single pass and those of INVENTION EXAMPLE 16 with two passes, higher ratios of surface resistance of the printed area to that of the non-printed area could be obtained, as can be seen from Table 5.

Table 5:

	Surface resistance of non-inked area [ $\Omega$ /square]				Surface resistance of inked areas [ $\Omega$ /square]			
	15s	30s	40s	60s	15s	30s	40s	60s
<b>Invention Example Nr. 15</b>								
90°C	-	$10^7$	$10^7$	$10^7$	-	$10^{9.5}$	$10^{10}$	$10^{10}$
110°C	$10^7$	$10^7$	-	$10^7$	$10^{10}$	$10^{10}$	-	$10^{10}$
<b>Invention Example Nr. 16</b>								
90°C	-	$10^6$	$10^6$	$10^6$	-	$10^8$	$10^8$	$10^9$
110°C	$10^6$	$10^6$	-	$10^5$	$10^9$	$10^9$	-	$10^9$

The best heating conditions were found to be 60s at 110°C. This produced a ratio of surface resistance of the printed area to that of the non-printed area for the twice printed print of INVENTION EXAMPLE 16 of  $10^4$ .

#### INVENTION EXAMPLE 20 and COMPARATIVE EXAMPLE 7

INVENTION EXAMPLE 20 and COMPARATIVE EXAMPLE 7 were carried out as described for INVENTION EXAMPLES 1 to 3 and COMPARATIVE EXAMPLE 1 except that the printing ink used was either NOVAVIT gelb 1 F 713, a yellow offset ink from BASF, or no printing ink was used at all, printing plate nr. 3 was used, the receiving media used were type 1 and the aqueous fountain media AFM03 was used as specified for INVENTION EXAMPLE 20 and for COMPARATIVE EXAMPLE 7 in Table 6.

30 sheets of the receiving medium were printed in each case and the surface resistances of the "inked" and "non-inked" areas measured with a two point method as described for INVENTION EXAMPLES 1 to 3 and COMPARATIVE EXAMPLE 1. The surface resistances of the inked and non-inked areas are also given in Table 6.

Table 6:

Print nr	Use of NOVAVIT gelb 1 F 713	receiving medium nr.	Surface resistance of inked area [ $\Omega$ /square]	Surface resistance of non-inked areas [ $\Omega$ /square]
<b>Comparative Example nr. 7</b>				
1	no	2	$10^{10}$	$10^8$
5	no	2	$10^{10}$	$10^9$
10	no	2	$10^9$	$10^9$
15	no	2	$10^9$	$10^9$
<b>Invention Example nr. 20</b>				
1	yes	2	$10^{10}$	$10^8$
5	yes	2	$10^{11}$	$10^8$
10	yes	2	$10^{11}$	$10^8$
15	yes	2	$10^{11}$	$10^8$

10 The evolution of conductivity differentiation between areas of the prints corresponding to the image and non-image areas of the printing plate for INVENTION EXAMPLE 20 using the NOVAVIT™ gelb 1 F 13 ink and aqueous fountain medium AFM03 showed that the conductivity differentiation increased with the number of prints up to 5 prints and then stabilized, whereas the conductivity differentiation between areas of the prints corresponding to the image and non-image areas of the printing plate in the case of COMPARATIVE EXAMPLE 7 in which only the aqueous fountain medium AFM03 was used no conductivity differentiation was observed from the 10th print.

This showed that any conductivity differentiation simply due to different affinity of the aqueous fountain medium for hydrophilic areas on the printing plate was rapidly lost during a printing run, whereas in the presence of a printing ink a stable conductivity differentiation was realized once the printing was in regime, as taught by the present invention.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any



generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.



## CLAIMS

1. A process for the offset printing of a receiving medium with a conductive pattern comprising in any order the steps of:  
5 applying a printing ink to a printing plate and wetting said printing plate with an aqueous fountain medium containing a solution or a dispersion of an intrinsically conductive polymer.
- 10 2. Process according to claim 1, wherein said intrinsically conductive polymer is selected from the group consisting of polyanilines, polyaniline derivatives, polypyrroles, polypyrrole derivatives, polythiophenes and polythiophene derivatives.
- 15 3. Process according to claim 1 or 2, wherein said conductive polymer is a polymer or copolymer of a 3,4-dialkoxythiophene in which the two alkoxy groups may be the same or different or together represent an optionally substituted oxy-alkylene-oxy  
20 bridge.
4. Process according to claim 1, wherein said intrinsically conductive polymer is selected from the group consisting of:  
homopolymers of (3,4-methylenedioxy-thiophene), (3,4-  
25 methylenedioxythiophene) derivatives, (3,4-ethylenedioxythiophene), (3,4-ethylenedioxythiophene) derivatives, (3,4-propylenedioxythiophene), (3,4-(propylenedioxythiophene) derivatives, (3,4-butylenedioxythiophene) and (3,4-butylenedioxythiophene)  
30 derivatives and copolymers thereof.
5. Process according to any of the preceding claims, wherein said aqueous fountain medium further contains a polyanion.
- 35 6. Process according to claim 5, wherein said polyanion is poly(styrenesulfonate).
7. Process according to any of the preceding claims, wherein said aqueous fountain medium further contains a di- or polyhydroxy-  
40 and/or carboxy groups or amide or lactam group containing organic compound.

8. Process according to claim 7, wherein said di- or polyhydroxy- and/or carboxy groups or amide or lactam group containing organic compound is selected from the group consisting of 1,2-propandiol, propylene glycol, diethylene glycol, N-methyl pyrrolidinone and di(ethylene glycol)ethyl ether acetate.
9. Process according to claim 7 or 8, wherein said process further contains a step subsequent to printing in which said receiving medium within 10 minutes of printing is heated to a temperature of 100 to 250°C.
10. Process according to any of claims 1 to 6, wherein said aqueous fountain medium further contains an aprotic organic compound with a dielectric constant  $\geq 15$ .
11. Process according to claim 10, wherein said process further contains a step subsequent to printing in which said receiving medium within 10 minutes of printing is heated to a temperature of  $\leq 150^\circ\text{C}$ .
12. Process according to any of the preceding claims, wherein said aqueous fountain medium further contains a non-ionic or anionic surfactant.
13. Process according to any of the preceding claims, wherein said aqueous fountain medium has a viscosity at 25°C after stirring to constant viscosity of 30 mPa.s as measured according to DIN 53211.
14. Process according to any of the preceding claims, wherein said aqueous fountain medium contains a dye and/or a pigment such that the colour tone of the ink and the background cannot be distinguished by the human.
15. Process according to any of the preceding claims, wherein said printing ink further contains a dye and/or a pigment such that the colour tone of the ink and the background cannot be distinguished by the human eye.

## ABSTRACT

PROCESS FOR THE OFFSET PRINTING OF PATTERNS OF INTRINSICALLY  
CONDUCTIVE POLYMERS

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A process for the offset printing of a receiving medium with a  
conductive pattern comprising in any order the steps of: applying a  
printing ink to a printing plate and wetting the printing plate  
with an aqueous fountain medium containing a solution or a  
10 dispersion of an intrinsically conductive polymer.

